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(54) Title: ODOR ELIMINATING AQUEOUS FORMULATION			
(57) Abstract  A deodorizing composition formed by an aqueous solution of divalent metal ions, preferably zinc ions, and i) an anionic alkylaryl alkoxy carboxylate/carboxylic acid surfactant and/or ii) an anionic alcohol alkoxy carboxylate/carboxylic acid surfactant.			

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## ODOR ELIMINATING AQUEOUS FORMULATION

Technical Field

5           The present invention relates to as aqueous formulation that substantially reduces odors. In particular, the invention relates to an aqueous solution of divalent metal ions, most preferably zinc ions, and an anionic alkoxy carboxylate/carboxylic acid surfactant.

Background Art

10           Offensive odors are a common problem. For example, offensive odors can emanate from contaminant materials, decaying materials, or incompatible materials. Even when  
15           such materials have been substantially removed, offensive odors can continue to be noticeable because of the high olfactory sensitivity of people. Further, offensive odors are caused by a variety of materials in a variety of environments. Thus, different deodorizing applications have  
20           varying requirements. Accordingly, there is a continuing need for deodorizing compositions to substantially eliminate offensive odors.

          Attempts to ameliorate offensive odors include the use of perfumes to mask such malodors. U.S. Patent No.  
25           3,490,982 describes a cosmetic microemulsion compositions that is formed by two immiscible liquid phases containing isoeicosane, water, a fragrance, and a fatty glyceride ester alkoxyated with alkylene oxide such as alkylene oxide alkoxyated caprylic/capric fatty glyceride ester. U.S.  
30           Patent No. 4,938,416 describes a water based fragrance dispersion that includes a fragrance oil and a fragrance enhancer such as an alcohol, ester, ketone, aldehyde, acid, terpene, ether, or other complex materials. A preferable nonionic surfactant such as nonylphenol polyoxyethylene or  
35           polyoxyethylene sorbitan monooleate can be included.

          Other attempts to form a composition that deodorizes include U.S. Patent No. 5,076,960 which describes an aqueous

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composition containing alkali metal halogenites such as sodium chlorite, a salt of a transition or post transition metal such as zinc chloride, and an alcohol to assist in stabilizing the sodium chlorite. The composition can include a perfume, in which case the perfume can be stabilized against the alkali metal halogenite by the use of an anionic surfactant. U.S. Patent No. 4,963,287 also describes a cleaner composition which includes an alkali metal halogenite, a perfume, and an anionic surfactant to stabilize the perfume. International Patent Publication WO 95/15186 and European Patent Publication EP 0 401 140 B1 describe deodorizing compositions containing aldehydes.

U.S. Patent No. 4,840,792 describes a composition for neutralizing bad smells utilizing a compound that is an aliphatic alcohol, aldehyde, aliphatic ketone, aliphatic ester, aromatic lactone, phenol, aromatic ether, amine, or an aromatic amine. U.S. Patent Nos. 4,946,672 and 4,818,524 describe deodorizing compositions containing imino (HN=) moieties such a polymeric biguanide. U.S. Patent No. 3,172,817 describes deodorizing compositions containing a beta-diketone.

British Patent No. 941,105, and U.S. Patent Nos. 2,544,093, and 3,074,891 describe deodorizing compositions containing esters of alpha,beta-unsaturated monocarboxylic acids. U.S. Patent No. 5,089,258 describes deodorizing compositions containing citric acid and a monovalent salt of citric acid. U.S. Patent No. 5,211,870 describes deodorizing compositions containing a zeolite. International Patent Publication No. WO 91/12029 describes deodorizing compositions containing zeolite and an absorbent gelling material.

U.S. Patent No. 4,983,578 describes deodorizing compositions containing hydroxyphosphoric acid, polyalkylene glycol alkyl ether, alcohol, and perfume. U.S. Patent No. 4,909,986 describes aqueous deodorizing compositions containing a water-soluble organic polymer having a carboxyl group and its ammonium salt. Organic monobasic acids and

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their salts may be included. The salts may include alkali metal salts, calcium salts, iron salts, ammonium salts and alkanol/alkanol-amine salts.

Insect repellents can present unpleasant odors.

5 Further, repellents can be more effective if the applied surface is better coated. Accordingly, repellent compositions can contain perfumes and surfactants. U.S. Patent Nos. 4,696,676, 4,933,371, and 5,196,200 describe repellents formed from alcohols such as 1-nonen-3-ol and  
10 linalool, while U.S. Patent No. 4,449,987 describes a fragrant insect repellent composition that includes methyl heptenone, coumarin, and an indole. Perfumes and surfactants may be included in these insect repellent compositions.

15 European Patent Publication 0 386 714 describes the use of monoterpenes such as borneol, isoborneol, camphor, and isobornyl acetate as a deodorizer and insect repellent.

Deodorants can be in the form of an aerosol composition. U.S. Patent No. 3,159,535 describes an aerosol  
20 composition that is a liquid/liquid/gas three phase composition which includes an emulsifier which can be anionic, cationic or nonionic. Particularly suitable emulsifiers include long chain fatty acid esters of polyhydrocyclic compounds such as the glycol, glycerol and  
25 sorbitol esters of oleic, stearic, palmitic and lauric acids; and ethoxylated fatty acids and amides. U.S. Patent No. 3,974,270 describes an aerosol composition using a water soluble poly-lower alkoxyated cetyl alcohol such as cetyl propoxylate as a vehicle for aluminum chlorhydrate.  
30 European Patent Publication No. 0 032 779 describes water-based aerosol compositions containing dimethylether, perfume, and an ethylene oxide/propylene oxide block copolymer surfactant.

Zinc compounds have been used in oral and dental  
35 compositions to reduce calculus formation and to inhibit offensive mouth odors. U.S. Patent No. 4,469,674 describes a composition containing zinc salt and a soluble ionic

fluoride salt. U.S. Patent No. 4,325,939 describes a composition containing an alkali metal zinc citrate or ammonium zinc citrate.

U.S. Patent No. 4,138,477 describes a composition, to  
5 control mouth odors, containing a combination formed from a zinc salt and an anionic polymer. The anionic polymer includes carboxyl, sulfonic or phosphonic acid groups with which the zinc ion reacts.

Many attempts to control odor utilize cyclodextrin or  
10 derivatives of cyclodextrin. U.S. Patent Nos. 3,486,011, 3,453,257, 3,453,258, 3,553,191, 3,565,887, 4,535,152, 4,638,258, 4,616,008, 4,678,598, 4,727,824, 4,746,734, 5,102,564, 5,234,610, 5,234,611, 5,578,563, 5,593,670, 5,663,134, 5,668,097, 5,714,137, 5,783,544, Japanese Patent  
15 Nos. JP 58-124452, JP 61-128973, JP 63-164953, JP 3-170415, JP 2-251681, JP 1-256597, JP 1-256596, and JP 3-284616, and International Patent Publications WO 89/02698 and WO 96/04940 describe particular perfumes, cyclodextrins, derivatives of cyclodextrin, and various compositions  
20 containing cyclodextrins, and/or its derivatives. Additional ingredients such as metallic salts such as zinc salts, anionic polymeric soil release agents, alkali carbonates and bicarbonates, clays, and surfactants are also described. U.S. Patent 5,663,134 states, however, that when  
25 metallic salts such as zinc salts are utilized, anionic surfactants are not preferred because water-insoluble salts can form.

As described above, surfactants are desirably included in deodorizing compositions used for many applications to  
30 assist in forming a complete, uniform coverage of the malodorous substrate by the applied composition. Surfactants can be described as cationic, nonionic, or anionic in accordance with their ionic properties, well known to one in the art. Anionic surfactants have a  
35 negative valence charge and are generally provided in association with a cation. When divalent cationic zinc is used in deodorizing compositions, nonionic or cationic

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surfactants are conventionally used in order to assure that the zinc ions remain in solution.

U.S. Patent No. 4,902,434 describes a dry granular composition, for the neutralization of odors and the removal of soil, formed from a divalent transition metal salt coated onto a solid inorganic granular carrier effective to bound malodorous materials to the surface of the carrier which then can be removed along with the dry granular carrier. Anionic surfactants such as sodium lauryl sulfate and magnesium lauryl sulfate can be used.

Without being bound to theory, it is believed that zinc ions in solution are more readily available to react with malodorous odor molecules than are zinc ions in a solid form (as a salt). Accordingly, it would be desirable to form a deodorizing composition that contains zinc ions in aqueous solution, together with an anionic surfactant that imparts improved flow and coating properties to the solution while maintaining the zinc ions in solution, to facilitate reactions of the zinc with malodorous molecules.

#### Disclosure of Invention

The present invention is directed to a deodorizing composition comprising an aqueous solution of divalent metal ions, preferably zinc ions, and an anionic surfactant. The anionic surfactant is described by the formula  $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$ , wherein R is a fatty alcohol substituent or an alkylaryl substituent. The fatty alcohol substituent is a residue of a  $C_6-C_{20}$  fatty alcohol, the alkylaryl substituent is a residue of a  $C_{10}-C_{20}$  alkylaryl compound, and X is at least 2. The metal divalent metal ions are present in a concentration that is effective to deodorize a substrate to which the solution is applied. The anionic surfactant is present in a concentration effective to maintain the metal ions in solution.

The aqueous solution of this invention advantageously may be a clear solution that can be formulated so that its application to a substrate in a deodorizing effective amount

does not leave a visible residue on the substrate.

The invention is also directed to a method to deodorize a substrate, comprising the step of applying the above-described deodorizing composition.

5

#### Modes of Carrying Out The Invention

The present invention is directed to a deodorizing composition that is an aqueous solution containing divalent metal ions and an anionic surfactant. The divalent metal  
10 ions are preferably copper or zinc, and most preferably zinc ions. The anionic surfactant is described by the formula  $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$ , wherein R is a fatty alcohol substituent or an alkylaryl substituent.

There should be at least two moles of the ethoxylate  
15 for each mole of surfactant molecule - that is, X should be at least 2. Preferably, X is from 2 to 20, most preferably, X is from 5 to 15.

When R is a fatty acid substituent, R should contain from 6 to 20 carbon atoms - that is, R should be formed from  
20 a  $C_6-C_{20}$  fatty alcohol. The fatty alcohol substituent provides hydrophobic functionality to the surfactant, balancing the hydrophilic functionality of the poly(ethylene oxide) carboxylate. Surfactants containing fatty alcohol substituents having carbon numbers below 6 disadvantageously  
25 are unlikely to provide adequate film forming and surface wetting properties.

When R is an alkylaryl substituent, the alkyl  
portion(s) should contain from 4 to 14 carbon atoms - that  
is, the overall alkylaryl substituent should be a  $C_{10}-C_{20}$   
30 substituent.

The anionic surfactant described by the formula  $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$ , wherein R is a fatty alcohol substituent, can be called an alcohol ethoxycarboxylate. The alcohol ethoxycarboxylate can be supplied associated with any  
35 convenient cation such as for example,  $H^+$ ,  $Na^+$ ,  $K^+$ , or  $NH_4^+$ . Any suitable convenient alcohol ethoxycarboxylic acid or alcohol ethoxycarboxylate can be used such as, for example,



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NEODOX™ alcohol ethoxycarboxylic acids from Shell Chemicals, Houston, Texas, and SANDOPAN® carboxylated surfactants from Clariant Corporation, Charlotte, North Carolina.

The anionic surfactant described by the formula  $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$ , wherein R is an alkylaryl substituent can be called an alkylaryl ethoxycarboxylate. The alkylaryl ethoxycarboxylate can be supplied associated with any convenient cation such as for example,  $H^+$ ,  $Na^+$ ,  $K^+$ , or  $NH_4^+$ . Any suitable convenient alkylaryl ethoxycarboxylic acid or alkylaryl ethoxycarboxylate can be used such as, for example, SANDOPAN® MA-18 carboxylated surfactants from Clariant Corporation, Charlotte, North Carolina.

The preferred divalent zinc ions can be supplied by any convenient source such as, for example, zinc chloride, zinc acetate, zinc bromide, zinc acetate, zinc salicylate, zinc propionate, zinc gluconate, zinc lactate, zinc maleate, zinc sulfate or zinc nitrate.

The zinc ions should be in the amount of from about 0.01 wt% to about 5 wt% of the total aqueous deodorizing composition. Preferably, the zinc ions should be in the amount of from about 0.02 wt% to about 2 wt%, more preferably from about 0.03 wt% to about 0.3 wt%. All percentages recited herein are weight percentages unless specifically stated otherwise.

The required anionic surfactant(s) used in the inventive composition advantageously provides multiple functions: i) as an emulsifier for added fragrance ingredients, ii) as a wetting agent, iii) as a control release agent for the zinc, and iv) as a deodorizer itself.

The first two properties are apparent. In regard to the third property, without being held to theory, it is believed that the control release agent properties of the surfactants of the present invention derive from the interaction of the anionic surfactant with the zinc +2 cation. It is believed that the zinc is lightly bound (weakly chelated) to the anionic surfactant. Thus, the zinc is sufficiently bound to maintain its solubility, yet sufficiently weakly bound so as

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to be available for reaction with malodorous molecules. It is believed that zinc reacts with the reduced sulfur compounds, such as thiols and disulfides, and amines that are often present as malodorous molecules. The zinc binds  
5 with the malodorous molecules to lower the volatility of the malodorous molecules, thus reducing and eliminating odor. Further, the anionic surfactant itself can react with malodorous molecules such as amines to reduce odor.

The pH of the aqueous composition of this invention  
10 should be acidic to about very slightly basic. Preferably, the pH should be from about 3 to about 8. More preferably, the pH should be from about 4 to about 7. Most preferably, the pH should be from about 4 to about 6. In general, a lower pH helps maintain solubilization and availability of  
15 the zinc cation.

Accordingly, another important function of the acid form of the anionic surfactants of the invention is to adjust the pH of the aqueous solution. The anionic surfactants of the invention can be used as a mixture of  
20 suitable anionic surfactants. Thus, a mixture of ethoxylated carboxylic acids and ethoxylated carboxylates can be used to conveniently adjust and control the solution pH. For example, a 1:1 mixture of SANDOPAN<sup>®</sup> DTC acid and SANDOPAN<sup>®</sup> LS-24-N have been conveniently used to control pH  
25 at about 5 or below.

The weight ratio of zinc to surfactant should be from about 1:2 to about 1:40. The anionic surfactant of the present invention should be from about 0.005 wt% to about 10 wt% of the total aqueous solution. Preferably, the anionic  
30 surfactant should be from about 0.2 wt% to about 1.0 wt%, and more preferably from about 0.50 wt% to about 0.75 wt%.

Other compatible constituents can be included in the aqueous formulations of this invention. Perfumes can be included to mask odors and to impart a pleasant fragrance to  
35 the solution. Miscible cosolvents such as, for example, isopropyl alcohol (isopropanol), ethanol, propylene glycol, or mixtures thereof can be included. Such cosolvents

conveniently include, for example, glycol ethers such as R-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>x</sub>OH, wherein R is a methyl, ethyl, propyl, butyl or hexyl substituent, and x is 1 or 2, and the corresponding propylene oxide based glycol ethers represented by the formula R-(OCH(CH<sub>3</sub>)CH<sub>2</sub>)<sub>x</sub>OH, wherein R is a methyl, ethyl, propyl, butyl or hexyl substituent, and x is 1 or 2. Such cosolvents can be included, for example, to assist in drying of the applied solution. Compatible colorants can be included to impart a pleasing color or to identify areas that have been treated with the aqueous solution. Various organic and inorganic acids may be included for pH control. Any other suitable compatible additive can be conveniently included such as, for example, preservatives, antifungal agents, and bacterial control agents.

#### Examples

The Examples which follow are intended as an illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied.

The aqueous solutions of the invention were tested against common malodors (smoke, pet smells, cooking odors, and mildew). The tests were performed over 24 hour periods.

A rating was made on a scale of 1-5 where 1 represents the odor totally removed, while 5 represents the odor unchanged.

Averages were calculated of the ratings after 5 minutes, 20 minutes, and 24 hours. The present invention was efficacious in all cases, exhibiting an average rating of about 2 or lower.

#### Examples 1-4

In Examples 1-4, SANDOPAN<sup>®</sup> LS-24-N (Clariant Corp.), a sodium laureth-13-carboxylate anionic surfactant, was warmed to 50°C. Then, SANDOPAN<sup>®</sup> DTC (Clariant Corp.), a trideceth-7-carboxylic acid anionic surfactant, was mixed in at a weight ratio of 1:2 LS-24-N:DTC to form an anionic surfactant mixture. Next, a compatible perfume was added to the anionic surfactant mixture at a weight ratio of at least 1:5

perfume:surfactant to form an anionic surfactant/perfume mixture.

5 Separately, water, isopropanol, and propylene glycol were mixed together with a quantity of the previously formed anionic surfactant/perfume mixture. Zinc chloride was then added to form the formulations (in wt%) shown in the table below. In these examples, the pH were approximately 4.3-4.5 and the final solutions were clear.

	Example			
	1	2	3	4
Zinc Chloride	0.05	0.5	1.0	1.5
IPA	2.0	2.0	5.0	7.0
Perfume	0.15	0.1	0.15	0.2
Total Surfactant	0.75	0.5	0.9	1.5
Propylene Glycol	0.05	0.05	0.00	0.00
Water	to Balance			

#### 10 Examples 5-9

15 In Examples 5-9, the solvents isopropyl alcohol (IPA) and propylene glycol were added to water under slow stirring. The perfume and surfactants were then added as a premixed liquid similarly as in Example 1, while stirring, until dissolved. The zinc chloride was then added. The pH was below 5 in each example. The formulations are shown in wt% (with the balance water) in the table below.

	Example				
	5	6	7	8	9
Citric Acid	0.1	0.2	0.2	0.2	0.2
Sodium Citrate	2.32	---	2.0	2.0	2.0
Zinc Chloride	0.05	0.01	0.05	0.1	0.5
IPA	2.0	2.0	2.0	2.0	2.0
Propylene Glycol	0.05	0.05	0.05	0.05	0.05
Perfume	0.1	0.1	0.1	0.1	0.1
Total Surfactant	0.9	0.9	0.9	0.9	0.9

#### Example 10 and 11

In Example 10, 1 wt% of a 1:1 LS-24-N to DTC surfactant mixture, 0.5 wt% fragrance, 5.0 wt% ethanol, and 0.5 wt% zinc chloride was added in that order to tap water while slowly stirring to form an effective deodorizing solution.

In Example 11, a solution was made similarly as in Example 10 but sodium citrate and citric acid was added to control the pH to below 5.5.

#### Industrial Applicability

The aqueous solution of the invention can be applied by any convenient method such as, for example, by spraying, wiping, pouring, or dipping. The application can be from any convenient applicator such as, for example, a pump spray container, an aerosol spray container, a sponge, a cloth, a synthetic composite applicator, a bottle, or a tray.

Other variations and modifications of this invention will be apparent to those skilled in this art after careful study of this application. This invention is not to be limited except as set forth in the following claims.

## Claims:

1. A deodorizing composition comprising an aqueous solution of divalent metal ions in a deodorizing effective amount and an anionic surfactant in an amount effective to solubilize said divalent metal ions, wherein said anionic surfactant is described by the formula  $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$ , wherein R is a fatty alcohol substituent or an alkylaryl substituent, said fatty alcohol substituent is a residue of a  $C_6-C_{20}$  fatty alcohol, said alkylaryl substituent is a residue of a  $C_{10}-C_{20}$  alkylaryl compound, and wherein X is at least 2.
2. The deodorizing composition according to claim 1, wherein said divalent metal ions are divalent zinc ions.
3. The deodorizing composition according to claim 1 or 2, wherein said X is from 2 to 20.
4. The deodorizing composition according to claim 1 or 2, wherein said X is from 5 to 15.
5. The deodorizing composition according to claim 2, wherein said concentration of divalent zinc ions is from about 0.01 wt% to about 5 wt% of the total aqueous solution.
6. The deodorizing composition according to claim 2, wherein said concentration of divalent zinc ions is from about 0.02 wt% to about 2 wt% of the total aqueous solution.
7. The deodorizing composition according to claim 2, wherein said concentration of divalent zinc ions is from about 0.03 wt% to about 0.3 wt% of the total aqueous solution.
8. The deodorizing composition according to claim 1 or 2, wherein said concentration of said anionic surfactant is

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from about 0.005 wt% to about 10 wt% of the total aqueous solution.

5 9. The deodorizing composition according to claim 1 or 2, wherein said concentration of said anionic surfactant is from about 0.2 wt% to about 1.0 wt% of the total aqueous solution.

10 10. The deodorizing composition according to claim 1 or 2, wherein said concentration of said anionic surfactant is about 0.50 wt% to about 0.75 wt% of the total aqueous solution.

15 11. The deodorizing composition according to claim 1 or 2, wherein said aqueous solution further includes a miscible cosolvent.

20 12. The deodorizing composition according to claim 11, wherein said miscible cosolvent is ethanol, isopropanol, propylene glycol, or a glycol ether.

25 13. The deodorizing composition according to claim 11, wherein said miscible cosolvent is an ethylene oxide based glycol ether represented by the formula  $R-(OCH_2CH_2)_xOH$ , wherein R is a methyl, ethyl, propyl, butyl or hexyl substituent, and x is 1 or 2.

30 14. The deodorizing composition according to claim 11, wherein said miscible cosolvent is a propylene oxide based glycol ether represented by the formula  $R-(OCH(CH_3)CH_2)_xOH$ , wherein R is a methyl, ethyl, propyl, butyl or hexyl substituent, and x is 1 or 2.

35 15. The deodorizing composition according to claim 1 or 2, wherein said anionic surfactant is a carboxylate ion described by the formula  $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$ , and wherein

said carboxylate ion is formed from the associated salt of  $H^+$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$ , or mixtures thereof.

5 16. The deodorizing composition according to claim 1 or 2, wherein said aqueous solution has a pH from about 3 to about 8.

10 17. The deodorizing composition according to claim 1 or 2, wherein said aqueous solution has a pH from about 3 to about 7.

15 18. The deodorizing composition according to claim 1 or 2, wherein said aqueous solution has a pH from about 3 to about 6.

20 19. A method to deodorize a substrate, said method comprising the step of applying an aqueous solution to the substrate, wherein said aqueous solution comprises divalent metal ions in a deodorizing effective amount and an anionic surfactant in an amount effective to solubilize said metal ions, wherein said anionic surfactant is described by the formula  $R-(O-CH_2-CH_2)_x-O-CH_2COO^-$ , wherein R is a fatty alcohol substituent or an alkylaryl substituent, said fatty alcohol substituent is a residue of a  $C_6$ - $C_{20}$  fatty alcohol, said  
25 alkylaryl substituent is a residue of a  $C_{10}$ - $C_{20}$  alkylaryl compound, and wherein X is at least 2.

20. The method according to claim 19 wherein said divalent ions are zinc ions.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/28441

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L9/01

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L A61K C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 09, 31 October 1995 (1995-10-31) & JP 07 165544 A (LION CORP), 27 June 1995 (1995-06-27) abstract	1, 2, 5, 8-10, 16-20
X	US 5 663 134 A (TRINH TOAN ET AL) 2 September 1997 (1997-09-02) cited in the application column 10, line 47 - column 11, line 13 column 11, line 35 - line 67 column 12, line 4 - line 21  -/-	1-6, 8-13, 15-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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